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## PROVISIONAL SPECIFICATION

## Degradation of Aromatic Linear Polyesters

We, ROYDEN LEWIS HEATH, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention to be as follows:

This invention relates to the degradation of aromatic polyesters.

The aromatic polyesters with which the present invention is concerned are the highly polymeric linear esters obtainable by heating glycols of the series  $\text{HO}(\text{CH}_2)_n\text{OH}$ , where  $n$  is an integer greater than 1 but not exceeding 10, with terephthalic acid or with an ester-forming derivative thereof, for example, an aliphatic (including cycloaliphatic) or aryl ester or half-ester, an acid halide or an ammonium or amine salt, under conditions which yield the esters in a highly polymerised condition. Examples of such highly polymeric linear esters are those obtainable from terephthalic acid or an ester-forming derivative thereof and ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol. These polyesters are high melting, difficultly soluble, colourless or substantially colourless materials which can be formed into filaments which can be extended by drawing into strong flexible fibres showing, by characteristic X-ray patterns, molecular orientation along the fibre axis. Of these polyesters, polyethylene terephthalate is preferred on account of its ready availability and of its outstanding utility as a textile material.

For many purposes it is required to degrade these aromatic polyesters, for example, to facilitate their removal from difficultly accessible vessels, in the recovery of scrap or in the recovery of terephthalic acid therefrom.

The present invention is directed to a means for degrading the aromatic polyesters.

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According to the present invention there is provided a process for the degradation of aromatic polyesters of the kind hereinbefore specified which comprises heating said polyesters with the glycol used in the manufacture of the polyesters to be degraded or with a terephthalate of said glycol or with a low molecular weight polyester formed from such terephthalate.

The degraded polyesters obtained according to the process of this invention may be reconverted by conventional methods into higher molecular weight polyesters or, alternatively, they may be further degraded, for example, by hydrolysis with an aqueous hydrolysing medium such as a dilute aqueous alkali or acid.

The degradation may be effected in a number of ways. For instance, the polyester may be heated with many proportions of the glycol until a homogeneous fluid mass is obtained. Alternatively, the polyester may be heated with a quantity of the glycol terephthalate or with a low molecular weight polyester formed therefrom until a homogeneous fluid mass is obtained. The fluid mass thus obtainable may thereafter be subjected to a heat treatment whereby a higher molecular weight polyester is formed, may be subjected to a further degradative treatment, or it may be cooled thus causing the degraded material to separate out, often in a crystalline form.

The invention is illustrated but not limited by the following Examples in which the parts are expressed by weight:

## EXAMPLE 1

5 parts of scrap undrawn yarn formed from polyethylene terephthalate are gently boiled with 100 parts of ethylene glycol in a vessel fitted with a reflux condenser. After 2 hours, the polyester is completely dissolved. The homogeneous liquid thus obtained is filtered whilst hot: it contains the degraded polyester.

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The so obtained degraded polyester may be converted into a high molecular weight polyester by heating this solution at a pressure of 30-40 mm. of mercury under conditions whereby excess of glycol is removed, and then heating the so obtained mass at 275°C. at a pressure of about 0.3 mm. of mercury, until the melt can be formed into filaments which can be drawn out into fibres.

#### EXAMPLE 2

The recipe of Example 1 is repeated except that drawn yarn is used in place

of the undrawn yarn. Similar results are obtained. 15

#### EXAMPLE 3

The recipe of Example 1 is repeated until the stage at which the homogeneous liquid is obtained. This liquid is cooled, whereupon a crystalline mass of glycol terephthalate separates. This ester can be further purified, if desired, by crystallisation from hot water. 20

Dated the 28th day of March, 1946.

E. A. BINGEN,

Solicitor for the Applicants.

### COMPLETE SPECIFICATION

#### Degradation of Aromatic Linear Polyesters

We, ROYDEN LEWIS HEATH, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to the degradation of aromatic polyesters.

The aromatic polyesters with which the present invention is concerned are the highly polymeric linear esters obtainable by heating glycols of the series  $\text{HO}(\text{CH}_2)_n\text{OH}$ , where  $n$  is an integer greater than 1 but not exceeding 10, with terephthalic acid or with an ester-forming derivative thereof, for example, an aliphatic (including cycloaliphatic) or aryl ester or half-ester, an acid halide or an ammonium or amine salt, under conditions which yield the esters in a highly polymerised condition. Examples of such highly polymeric linear esters are those obtainable from terephthalic acid or an ester-forming derivative thereof and ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol. These polyesters are high melting, difficulty soluble, colourless or substantially colourless materials which can be formed into filaments which can be extended by drawing into strong flexible fibres showing, by characteristic X-ray patterns, molecular orientation along the fibre axis. Of these polyesters, polyethylene terephthalate is preferred on account of its ready availability and of its outstanding utility as a textile material.

For many purposes it is required to degrade these aromatic polyesters, for

example, to facilitate their removal from difficultly accessible vessels, in the recovery of scrap or in the recovery of terephthalic acid therefrom. 75

The present invention is directed to a means for degrading the aromatic polyesters.

According to the present invention there is provided a process for the degradation of aromatic polyesters of the kind hereinbefore specified which comprises heating said polyesters with the glycol used in the manufacture of the polyesters to be degraded or with a terephthalate of said glycol or with a low molecular weight polyester formed from such terephthalate. 80

The degraded polyesters obtained according to the process of this invention may be reconverted by conventional methods into higher molecular weight polyesters or, alternatively, they may be further degraded, for example, by hydrolysis with an aqueous hydrolysing medium such as a dilute aqueous alkali or acid. 85

The degradation may be effected in a number of ways. For instance, the polyester may be heated with many proportions of the glycol until a homogeneous fluid mass is obtained. Alternatively, the polyester may be heated with a quantity of the glycol terephthalate or with a low molecular weight polyester formed therefrom until a homogeneous fluid mass is obtained. Usually, several proportions of the glycol terephthalate or a low molecular weight polyester formed therefrom are used. The fluid mass thus obtainable may thereafter be subjected to a heat treatment whereby a higher molecular weight polyester is formed, may be subjected to a further degradative treatment, or it may be cooled thus causing the degraded material to separate out, often in a crystalline form. If desired, the fluid 100 105 110 115

mass may be discarded.

The temperature of the heating for the purposes of the present invention is conveniently at or about the boiling point of the glycol or the derivative thereof under the conditions of operation.

The degradation operation may be effected at atmospheric or at reduced or elevated pressures, but operation at atmospheric or elevated pressures is preferred since this enables the heating to be effected at higher temperatures and thereby tends to speed up the rate of degradation and results in the formation of a homogeneous fluid mass in a relatively shorter time.

The degradation operation of the present invention is of outstanding utility for cleaning vessels, pipes or other plant from solid aromatic polyesters adhering thereto. For instance, plant which has been used for the manufacture of the aromatic polyesters, after the removal of the bulk of the aromatic polyester in molten form, is found on cooling to be more or less coated with and/or blocked up by a hard tenacious mass of the solid aromatic polyester. Hitherto, the removal of this hard tenacious mass has been a matter of considerable difficulty. A short heating of the hard tenacious mass with the glycol or derivative thereof, preferably at an elevated pressure, provides a simple, quick and economical means of cleaning such plant.

The invention is illustrated but not limited by the following Examples in which the parts are expressed by weight:

#### EXAMPLE 1

5 parts of scrap undrawn yarn formed from polyethylene terephthalate are gently boiled with 100 parts of ethylene glycol in a vessel fitted with a reflux condenser. After 2 hours, the polyester is completely dissolved. The homogeneous liquid thus obtained is filtered whilst hot; it contains the degraded polyester.

The so obtained degraded polyester may be converted into a high molecular weight polyester by heating this solution at a pressure of 30-40 mm. of mercury under conditions whereby excess of glycol is removed, and then heating the so obtained mass at 275°C. at a pressure of about 0.3 mm. of mercury, until the melt can be formed into filaments which can be drawn out into fibres.

#### EXAMPLE 2

The recipe of Example 1 is repeated except that drawn yarn is used in place

of the undrawn yarn. Similar results are obtained.

#### EXAMPLE 3

The recipe of Example 1 is repeated until the stage at which the homogeneous liquid is obtained. This liquid is cooled, whereupon a crystalline mass of ethylene glycol terephthalate separates. This ester can be further purified, if desired, by crystallisation from hot water.

The following Example is illustrative of the use of the process of the invention for cleaning plant containing solidified aromatic polyesters:—

#### EXAMPLE 4

An autoclave of capacity of 3 gallons and ancillary equipment, which has been used for the manufacture of a quantity of polyethylene terephthalate, and from which the batch has been removed as completely as is possible through a conventional extrusion valve at the base of the autoclave, is found, on cooling, to be coated on the inside with the solid polyester and, usually, much of the ancillary equipment and valves is blocked with the solid polyester. There is introduced into the autoclave about  $\frac{1}{2}$  gallon of ethylene glycol and the autoclave and contents are heated so that the glycol boils under reflux conditions. After heating for about 2 hours the autoclave and its attachments are entirely cleaned from the solid polyester, and a fluid mass is obtained which can readily be removed through the extrusion valve.

When the heating with the ethylene glycol is effected in a closed system, thus enabling the heating to be at an elevated pressure and at a higher temperature, heating for from several minutes up to not more than half an hour usually suffices to give a homogeneous fluid mass and to provide an effective cleaning of the plant.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the degradation of aromatic polyesters of the kind hereinbefore specified which comprises heating said polyesters with the glycol used in the manufacture of the polyesters to be degraded or with a terephthalate of said glycol or with a low molecular weight polyester formed from such terephthalate.

2. A process as claimed in Claim 1, wherein the heating is at or about the boiling point of the glycol or the deriv-

ative thereof under the conditions of operation.

3. A process as claimed in either of the preceding Claims wherein the operation is effected at atmospheric or elevated pressures.

4. A process as claimed in any of the preceding Claims wherein the operation is used for cleaning vessels, pipes or other plant from solid aromatic polyesters adhering thereto.

5. A process as claimed in any of the preceding Claims wherein the aromatic

polyester is polyethylene terephthalate.

6. A process as hereinbefore particularly described and ascertained for the degradation of aromatic polyesters of the kind specified, with particular reference to the foregoing Examples. 15

7. Degraded aromatic polyesters whenever obtained by the process claimed in any of the preceding Claims. 20

Dated the 26th day of March, 1947.

E. A. BINGEN,  
Solicitor for the Applicants.

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